

Cooperative electron-phonon interaction in molecular chains

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Using a controlled analytic treatment, we derive a model that generically describes cooperative strong electron-phonon interaction (EPI) in one-band and two-band Jahn-Teller (JT) systems. The model involves a *next-nearest-neighbor* hopping and a nearest-neighbor repulsion. Rings with odd number of sites (o-rings) belong to a different universality class compared to rings with even number (e-rings). The e-rings, upon tuning repulsion, undergo a dramatic discontinuous transition to a *conducting commensurate* charge density wave (CDW) state with a period independent of filling.

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The last few decades have witnessed numerous studies to fathom the tapestry of exotic orbital, charge, and spin orderings in JT transition metal oxides (TMO) such as the manganites, cuprates, nickelates, etc. [1]. To model the emergent ordering in these complex TMOs, one needs, as building blocks, effective Hamiltonians for various interactions. Except for the cooperative JT interaction, effective Hamiltonians, that reasonably mimic the physics, have been derived for all other interactions. For instance, double exchange model approximates infinite Hund's coupling, Gutzwiller approximation or dynamical mean-field theory model Hubbard on-site coulombic interaction, superexchange describes localized spin interaction at strong on-site repulsion, etc. Controlled mathematical modeling of cooperative JT quantum systems that goes beyond modeling localized carriers [2] has remained elusive (at least to our knowledge). In fact, a controlled analytic treatment of the many-polaron effects in single-band Holstein model [3] (which is a simpler non-cooperative EPI system) has been reported only recently [4]. However, definite progress has been made in numerically treating JT systems [1].

Owing to its cooperative nature, the JT interaction leads to non-local distortion effects which can change the very nature of long range order. The situation is further complicated by the ubiquitous strong EPI for which there is compelling evidence in manganites (from extended X-ray absorption fine structure [5] and pulsed neutron diffraction [6] measurements), in cuprates (through angle-resolved photoemission spectroscopy [7]), and in nickelates (based on neutron scattering [8]). While a weak interaction is amenable to a Migdal-type of perturbative treatment, the strong interaction (even for a single-band system) necessitates a non-perturbative approach [4].

In this letter, based on our work [4] on the Holstein model [Fig. 1(a)], we derive the effective Hamiltonian for cooperative strong EPI in one-band system [Fig. 1(b)] and two-band (from d_{z^2} and $d_{x^2-y^2}$ orbitals) JT chain [Fig. 1(c)]. Upon inclusion of cooperative effects in the strong EPI, the system changes its dominant transport mechanism from one of nearest-neighbor hopping to that

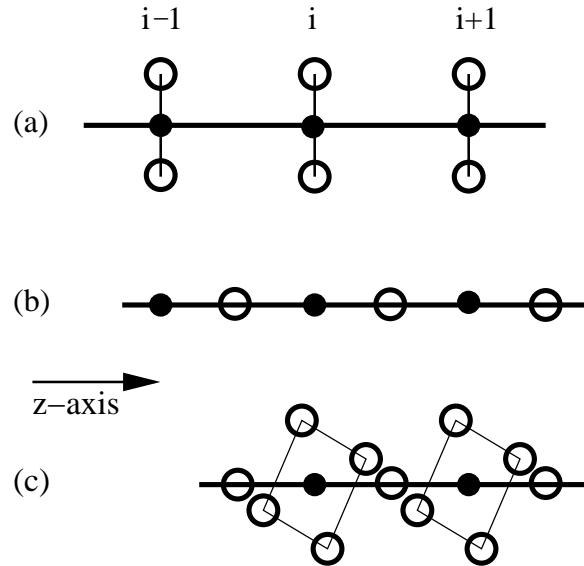


FIG. 1: Molecular chains with d_{z^2} orbital hopping sites (filled circles) and oxygen sites (empty circles) in (a) Holstein model, (b) one-band cooperative EPI system, and (c) two-band cooperative JT system with Q_1 , Q_2 , and Q_3 octahedral modes.

of next-nearest-neighbor hopping. Below half-filling and at strong EPI in e-rings, while the systems without cooperative effects remain disordered Luttinger liquids, our cooperative EPI one-band and two-band JT systems produce CDW states. Furthermore, *like the manganites, our JT system too manifests absence of electron-hole symmetry only upon including cooperative effects*.

To bring out the essential physics, we begin with a one-dimensional (1D) toy-system of electrons hopping in a one-band system of d_{z^2} orbitals which are coupled to the oxygens in between as shown in Fig. 1(b) [9]. The Hamiltonian is expressed as $H = H_t + H_{ep} + H_l$ where the hopping term H_t is given by

$$H_t = -t \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}), \quad (1)$$

with c_j being the destruction operator of an electron in

a $d_{z^2}^j$ orbital (at site j) and the EPI term H_{ep} by

$$H_{ep} = -g\omega_0 \sqrt{2M\omega_0} \sum_j n_j q_j, \quad (2)$$

with $n_i = c_i^\dagger c_i$, $q_i = u_i - u_{i-1}$ representing the expansion of the oxygens around the $d_{z^2}^j$ orbital, and the right-hand-side (RHS) oxygen displacement $u_i = (a_i^\dagger + a_i)/\sqrt{2M\omega_0}$. Furthermore, the lattice term H_l representing simple harmonic oscillators is of the form

$$H_l = \frac{K}{2} \sum_j u_j^2 + \frac{1}{2M} \sum_j p_j^2 = \omega_0 \sum_j a_j^\dagger a_j. \quad (3)$$

The main difference between the Holstein model and the above cooperative Hamiltonian is that in the Holstein model electrons at different sites are coupled to different on-site molecular distortions whereas in the present toy-system the electrons on adjacent sites are coupled to the displacement of the same in-between oxygen. Thus in our toy-system, to produce an effective polaronic Hamiltonian, we need to devise a modification of the usual Lang-Firsov transformation [10] so as to take into account the cooperative nature of the distortions. To meet this end we used the following canonical transformation $\tilde{H} = \exp(S)H\exp(-S)$ where S now contains the *difference in densities on adjacent sites*

$$S = g \sum_j (a_j - a_j^\dagger)(n_j - n_{j+1}). \quad (4)$$

Then, one obtains $\tilde{H} = H_0 + H_1$ where

$$H_0 = \omega_0 \sum_j a_j^\dagger a_j - 2g^2\omega_0 \sum_j n_j + 2g^2\omega_0 \sum_j n_j n_{j+1} - te^{-3g^2} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}), \quad (5)$$

and

$$H_1 = \sum_j H_{1j} = -te^{-3g^2} \sum_j [c_j^\dagger c_{j+1} \{T_+^{j\dagger} T_-^j - 1\} + \text{H.c.}],$$

with $T_\pm^j = \exp[\pm g(2a_j - a_{j-1} - a_{j+1})]$. On account of the cooperative nature of the EPI we obtain an additional term $2g^2\omega_0 \sum_j n_j n_{j+1}$ involving nearest-neighbor repulsion in H_0 and the perturbation H_1 now involves phonons at three sites as opposed to phonons at only two sites as in the non-cooperative case. We consider the case $t \exp[-3g^2] \ll \omega_0$ and perform second-order perturbation theory similar to that in Ref. 4. For large g^2 , after tedious algebra, we obtain the following effective polaronic Hamiltonian [11]:

$$H_{eff}^C = - \left[2g^2\omega_0 + \frac{t^2}{3g^2\omega_0} \right] \sum_j n_{j+1}(1 - n_j) - te^{-3g^2} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}) - \frac{t^2 e^{-2g^2}}{4g^2\omega_0} [c_{j-1}^\dagger (1 - 2n_j) c_{j+1} + \text{H.c.}] \quad (6)$$

Notice that the coefficient of the nearest-neighbor hopping is significantly smaller than the next-nearest-neighbor hopping for large g^2 and not-too-small t/ω_0 ! This is a *key feature resulting from cooperative effects*.

The above effective Hamiltonian may be contrasted with the following Hamiltonian H_{eff} for the case where there is no cooperative EPI [i.e., $H_{ep} = -\sqrt{2}g\omega_0 \sum_i n_i (a_i^\dagger + a_i)$] [see Ref. 4 and Fig. 1(a)]:

$$H_{eff} = -2g^2\omega_0 \sum_j n_j - \frac{t^2}{2g^2\omega_0} \sum_j n_{j+1}(1 - n_j) - te^{-2g^2} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}) - \frac{t^2 e^{-2g^2}}{2g^2\omega_0} \sum_j [c_{j-1}^\dagger (1 - 2n_j) c_{j+1} + \text{H.c.}] \quad (7)$$

Although our results in Eq. (7) are valid for $te^{-2g^2} \ll \omega_0$ and $g^2 \gg 1$, we provide an explanation of the results in the more restrictive but physically understandable adiabatic ($t \gg \omega_0$) and small polaronic ($g^2\omega_0 \gg t$) regime as follows. In Eq. (7), the coefficient of the $\sum_j n_{j+1}(1 - n_j)$ term can be understood as resulting from an adiabatic process when an electron at site $j+1$ hops to a neighboring site j and back, but the lattice has no time to distort (relax) *locally* at site j ($j+1$) and thus yields the second-order perturbation energy $-t^2$ /(energy change). On the other hand the coefficient of $\sum_j [c_{j-1}^\dagger (1 - 2n_j) c_{j+1} + \text{H.c.}]$ results when the intermediate site j does not distort/relax in an adiabatic hopping and thus yields $t \exp[-2g^2] \times \frac{t}{2g^2\omega_0}$ where $t \exp[-2g^2]$ is due to distortions at both initial and final sites $j-1$ and $j+1$. In the above non-cooperative case, the nearest-neighbor hopping dominates over the next-nearest-neighbor hopping in the small polaron limit.

Using the above logic we see that the higher order terms in perturbation theory, for both cooperative and non-cooperative cases, are dominated by the process where an electron hops back and forth between the same two sites. The dominant term to k th order is approximately given for even k by

$$\omega_0 \left[\frac{t}{g\omega_0} \right]^k \sum_j n_{j+1}(1 - n_j), \quad (8)$$

while for odd k by

$$te^{-\gamma g^2} \left[\frac{t}{g\omega_0} \right]^{k-1} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}), \quad (9)$$

where γ is 2 for the non-cooperative case and 3 for the cooperative one. Since each term in the perturbation theory should be smaller than ω_0 , we see that the small parameter in our perturbation is $t/(g\omega_0)$ [12].

Here, a few observations are in order. Firstly, the cooperative effects, unlike in the Holstein model's case, raise

the potential of the site next to an occupied site and thus makes it unfavorable for hopping. Thus, in Eq. (6) as compared to Eq. (7), the exponent is larger for the nearest-neighbor hopping and also the denominators of the coefficients are similarly larger for the hopping-generated nearest-neighbor interaction and for the next-nearest-neighbor hopping. Next, Lau *et al.* [9] obtain the same energy expression for a *single polaron* as that given by Eq. (6) (when $n_j = 0$). Lastly, in Ref. 13, the authors explain the ferromagnetic insulating behavior in low-doped manganites by using the non-cooperative hopping-generated nearest-neighbor interaction [i.e., second term on RHS of Eq. (7)] after modifying the hopping term for double-exchange effects. From Eq. (6), we see that cooperative phenomenon must be taken into account as it reduces the ferromagnetism generating interaction strength by a factor of 1.5.

We will now analyze the effective polaron Hamiltonian given by Eq. (6). We first note that, for large values of g^2 , the essential physics is captured by

$$H_{eff}^C = -T \sum_j (c_{j-1}^\dagger (1 - 2n_j) c_{j+1} + \text{H.c.}) + V \sum_j n_j n_{j+1}, \quad (10)$$

with $T/V \ll 1$. However, owing to its novelty, we will study the model given by Eq. (10) for arbitrary value of T/V . Next we note that for $T/V \ll 1$ in e-rings, the system always has alternate sites (one sub-lattice) occupied for less than half-filling and above half-filling the other sub-lattice gets filled. This is due to the fact that at large repulsion, as we fill up the lattice with electrons one after the other, each new electron added to the system has more number of sites to hop to on the same sub-lattice occupied by the previous electrons. As for the other extreme situation $V = 0$, for even number of electrons on e-rings, the model has both sub-lattices equally occupied.

Using modified Lanczos [14], we calculated the ground state energy using periodic (antiperiodic) boundary conditions for odd (even) number of fermions. First for *e-rings with N sites, the ground state energy has a slope discontinuity, with the energy increasing up to a critical value, after which it is constant* (see Fig. 2). We will now show clearly that as the interaction strength increases, *at a critical value of V/T , Ising Z_2 symmetry (i.e., both sub-lattices being equally populated) is broken and only a single sub-lattice is occupied for e-rings*. To this end, we calculate the density-density correlation function $W(l) = 4/N \sum_j \langle (n_j - 0.5)(n_{j+l} - 0.5) \rangle$ and the static structure factor $S(k) = \sum_l \exp(ikl)W(l)$ near critical value. Now, $S(\pi) = [\sum_{l \text{ even}} - \sum_{l \text{ odd}}]W(l)$ with

$$\sum_{l \text{ even}} W(l) = \frac{4}{N} \{ [N_e - 0.25N]^2 + [N_o - 0.25N]^2 \}, \quad (11)$$

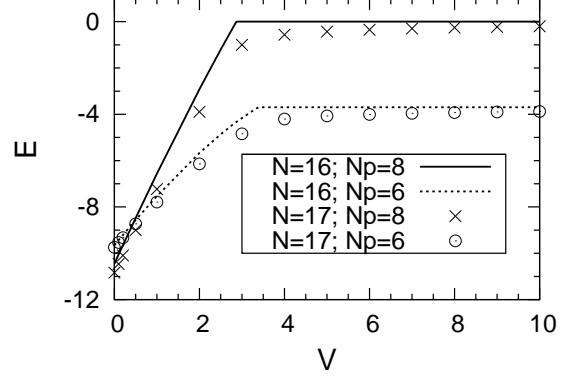


FIG. 2: Plots of Energy (E) versus interaction strength (V) for rings with N sites, N_p electrons, and hopping $T = 1$.

and

$$\sum_{l \text{ odd}} W(l) = \frac{8}{N} [N_e - 0.25N][N_o - 0.25N], \quad (12)$$

where $N_{e(o)}$ is the number of particles on even (odd) sites. Then, when Z_2 symmetry is respected, for even number of particles $N_p = 2N_e = 2N_o$, we have $S(\pi) = 0$ and for odd value of N_p we have $S(\pi) = 4/N$. When only one sub-lattice is occupied, on taking $N_e = N_p$ and $N_o = 0$ (without loss of generality), we get $S(\pi) = 4N_p^2/N$ and $W(l \text{ odd}) = 1 - 4N_p/N$. We find that at a critical interaction strength, as shown in Fig. 3, the following dramatic changes occur: (i) the structure factor $S(\pi)$ jumps from near 0 to almost its maximum value $4N_p^2/N$; (ii) $W(l \text{ odd})$ also jumps close to its large V value of $1 - 4N_p/N$; and (iii) $W(l \text{ even})$ (for $l \neq 0$) too jumps and its final value at half-filling is 1. For a fixed T and N , the critical value V_C^N of V increases monotonically as N_p decreases. For $N = 16$, $N_p = 2$, and $T = 1$, we get $V_C^{16} \approx 4$. From finite size scaling for half-filling, using $V_C^N - V_C^\infty \propto 1/N^2$ and system size $N \leq 20$, we obtain $V_C^\infty \approx 2.83$.

We see from the above analysis that, at a critical repulsion, the system undergoes a discontinuous transition to a *conducting commensurate CDW* state away from half-filling while at half-filling one obtains a Mott transition. Usually commensurate CDW's are insulating (see Ref. 15) whereas our model surprisingly predicts a conducting commensurate CDW. Furthermore, quite unlike the Peierls transition, the *period of the CDW is independent of density!* Such density independent charge ordering has indeed been observed in manganites (see Fig. 2 in Ref. 16). Our toy-system is different from the non-cooperative EPI Holstein model in that the latter, at strong coupling and finite t/ω_0 , can be mapped onto an anisotropic Heisenberg model and is thus always a Luttinger liquid away from half-filling (see Ref. 4).

We will now discuss o-rings for number of electrons less than half the number of sites. The case when the

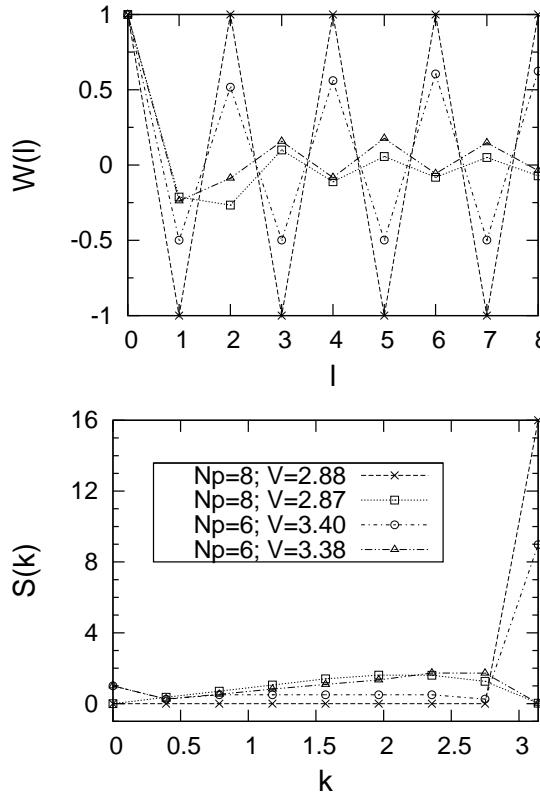


FIG. 3: Plot of the density-density correlation function $W(l)$ and structure factor $S(k)$ for a 16-site ring with N_p electrons, interaction strength V , and hopping $T = 1$.

number of electrons is greater can be deduced invoking electron-hole symmetry. Since the system has all sites connected through next-nearest-neighbor hopping (much like a Moebius strip), there do not exist 2 sub-lattices. Consequently, as the interaction increases, the system's energy increases monotonically and smoothly (without any slope discontinuities) and there is no phase transition [see Fig. 2]. We find that the system's energy increases linearly at small strengths as can be expected from a mean-filed analysis. At large values, the system's energy approaches asymptotically the energy of the e-ring with one less site but with the same number of electrons. This is because at large V , hard core repulsion on adjacent sites blocks electrons similar to Pauli's exclusion principle on the same site.

Lastly, for the 1D JT system shown in Fig. 1(c), we first note that there is a strong on-site inter-orbital repulsion given by $U \sum_j n_j n'_j$ where $U \rightarrow \infty$ and $n'_j = d_j^\dagger d_j$ with d being the destruction operator of a localized electron in a $d_{x^2-y^2}$ orbital. Next, like the one-band case [see Eq. (6)], the cooperative JT effect too produces strong nearest-neighbor repulsion $\propto g^2 \omega_0 \sum_j n_j n_{j+1}$. Again as before, there is a virtual-hopping generated nearest-neighbor repulsion term $-G \sum_{j,\delta=\pm 1} n_{j+\delta} (1-n_j) (1-n'_j)$ with the additional $(1-n'_j)$ factor prohibiting hopping

of a d_{z^2} electron to a neighboring j site if it is occupied by a $d_{x^2-y^2}$ electron. Here too $G \propto t^2/(g^2 \omega_0)$. Then, the Hamiltonian at large EPI (whose exact form is obtained after quite tedious algebra [11]) is essentially given by

$$H_{eff}^{CJT} = \sum_j [V n_j n_{j+1} + U n_j n'_j] - G \sum_{j,\delta=\pm 1} n_{j+\delta} (1-n'_j) - T \sum_j [(1-n'_j) c_{j-1}^\dagger (1-2n_j) c_{j+1} + \text{H.c.}], \quad (13)$$

with $G \gg T$. As in Eq. (10), here too V is an arbitrary variable. In Eq. (13), in the next-nearest-neighbor hopping term, the $(1-n'_j)$ factor does not allow hopping via the j site if it is occupied by a $d_{x^2-y^2}$ electron.

For fillings up to half (i.e., 0.5 electron/site), the electrons populate only the d_{z^2} orbitals (i.e., $n'_j = 0$) and the behavior of the above model of Eq. (13) is identical to that of the effective model given by Eq. (10) and is depicted by Fig. 2 when E is replaced by $E + 2N_p G$. Our results agree with the experimental observations that C-type ferromagnetic-chain manganites, like $Nd_{1-x}Sr_xMnO_3$ at $0.63 \leq x \leq 0.8$ [17], are d_{z^2} polarized. For fillings between half and unity and when $V \gg G$ (as in a real cooperative EPI system), for e-rings [o-rings] $N/2$ $[(N-1)/2]$ electrons populate d_{z^2} orbitals with the rest occupying $d_{x^2-y^2}$ orbitals; thus system lacks electron-hole symmetry.

On ignoring cooperative effects in our JT system of Fig. 1(c), in Eq. (13) we set $V = 2G$ and add a nearest-neighbor hopping $-T_0 \sum_{j,\delta=\pm 1} c_j^\dagger c_{j+\delta}$ with $G \gg T_0 \gg T$ [as in Eq. (7)]. Then, importantly, only d_{z^2} orbitals are occupied at any filling (up to unity) and the system exhibits electron-hole symmetry. Furthermore, since $n'_j = 0$, the system is always a Luttinger liquid at non-half-filling [4].

In summary, our study shows that cooperative EPI produces strikingly different physics compared to the non-cooperative situation. Our derived model captures the essential feature of cooperative strong EPI in all dimensions (and in even non-cubic geometries), i.e., the dominant transport is due to next-nearest-neighbor hopping. Our controlled analysis of cooperative JT interaction is currently being extended to higher dimensions.

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